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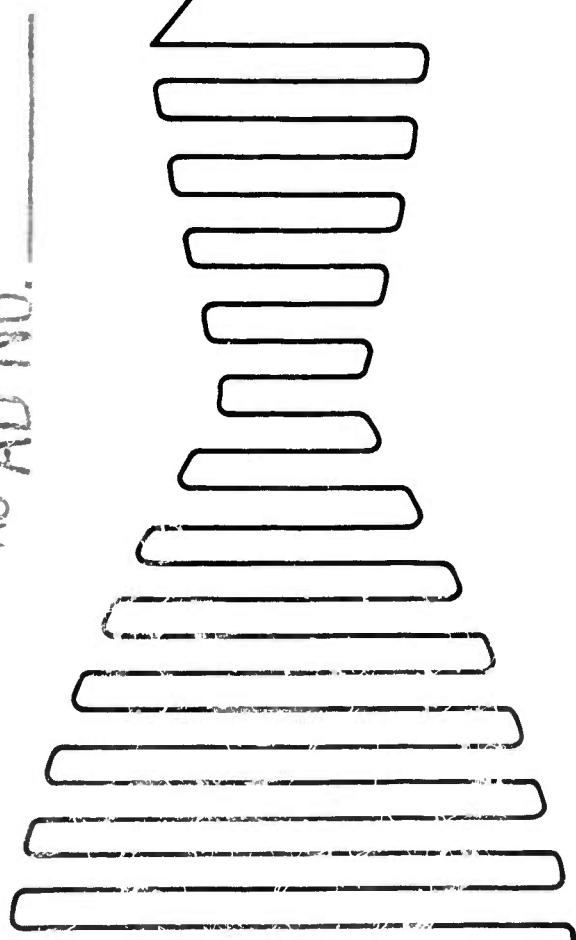
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(Unclassified Title)

49

RESEARCH ON FLUORINE OXIDIZERS,
QUARTERLY PROGRAM REPORT
FOR PERIOD ENDING 15 JUNE 1961

XEROX

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FOREWORD

This report was prepared by the Synthetic Chemistry Group of the Research Department of Rocketdyne. This research effort is supported by the Advanced Projects Research Agency under contract Nonr 3451(00).

The responsible scientist for this work is Dr. Emil A. Lawton. Dr. Walter Maya and Mr. David F. Sheehan are full-time associates, Dr. H. F. Bauer who joined the company during this reporting period is also now a full-time associate. Dr. Bart L. Tuffly and Mr. Virgil Bedwell conducted the mass spectral analysis and the gas chromatographic separations.

ABSTRACT

The reduction of pure NF_3O by iodide ion was found to give a value of 3 equivalents per mole, providing direct chemical evidence for its formula. The vapor pressure of NF_3O fits the equation: $\log p = 7.86279 - 917.087/T$, and the following quantities were derived: boiling point: -89.1 C, $\Delta H_v = 4195 \pm 26$ cal, Trouton's constant: 22.8. The melting point was also determined: -161.5 ± 1.0 C.

The previously reported compound, believed to be a new binary NF compound arising from the electrical discharge of fluorine-nitrogen mixtures, has also been synthesized from nitrogen trifluoride-nitrogen mixtures, but in too small a quantity for characterization as yet. The direct fluorination of trimethyl orthoformate at -80 C has given a complex mixture of products, which possess unassigned absorptions in the infrared between 10 and 13 microns. The reaction is being studied to determine if these absorptions are due to new oxidizers.

(Confidential Abstract)

R-3071-1

ii

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CONTENTS

Foreword	ii
Abstract	ii
Introduction	1
Discussion	2
Physical and Chemical Properties of NF_3^0	2
Synthesis of NF_3^0	4
Binary N-F Compounds	6
Direct Fluorinations	9
Experimental Details	11
Physical and Chemical Properties of NF_3^0	11
Preparation of NF_3^0	14
Binary N-F Compounds by Electrical Discharge	16
Direct Fluorinations	19
Summary and Conclusions	23
References	24

R-3071-1

iii

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ILLUSTRATIONS

1. Modified U Reactor	5
2. Infrared Spectrum of Mixture of Compounds Produced by Electrical Discharge	7
3. Gas Phase Fluorination Reactor	20
4. Fluorination Reactor for Low Temperatures	21

TABLES

1. Vapor Pressure of NF ₃ ⁰	13
2. Preparation of Compound A	17

R-3071-1

iv

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INTRODUCTION

The search for high-energy storable oxidizers has led Rocketdyne to concentrate on the synthesis of compounds containing mainly N-F and O-F bonds. The synthesis of these compounds has entailed new synthetic methods, among which the most fruitful have been direct fluorination and, more recently, the electrical discharge. In our hands, the electrical discharge has enabled us to synthesize NF₃O as well as two other compounds as yet not fully characterized. This report covers our efforts in the synthesis of new compounds by these methods and in the characterization of the physical and chemical properties of NF₃O.

R-3071-1

1

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DISCUSSION

PHYSICAL AND CHEMICAL PROPERTIES OF NF_3^0

It seems fairly certain now that the structure of NOF_3 is F_3NO and not NF_2OF . Evidence for this structure has been obtained by detailed infrared spectral analysis (Ref. 1) obtained in these laboratories, and by NMR studies (Ref. 2) done at the Allied Chemical Company. A detailed discussion of the structure of NF_3^0 will be found in Ref 1.

The successful purification of NF_3^0 by vapor phase chromatography (Ref. 1), together with improved synthetical methods that have allowed greater quantities of it to be available for study, have made possible the determination of physical properties. The NF_3^0 used in these measurements was free from N_2^0 , and had a purity better than 99 percent, determined both by mass spectral and infrared analysis.

Oxidation Equivalent

The reduction of NF_3^0 by acidic potassium iodide in water was determined to proceed according to the following equation:



The oxidation equivalent of NF_3^0 was found to be 3.2 equivalents per mole (calculated 3.0), and the nitric oxide was recovered and identified. The nitric oxide does not further oxidize iodide ion, but leads to slightly high values for the oxidation equivalent due to its conversion to nitrogen

R-3071-1

2

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dioxide by traces of oxygen. Since nitrogen dioxide is reduced by iodide ion in acidic solutions back to nitric oxide, a catalyzed reduction of iodide by air can easily take place. Therefore, extreme care was taken in avoiding contamination by oxygen during the reduction, and in removing the nitric oxide before the free iodine was titrated. This determination provides direct chemical evidence for the empirical formula NOF_3 .

Physical Properties of NF_3

The molecular weight of NF_3 was redetermined (Ref. 3) on a pure sample. Two determinations were done by the gas density method, and a value of 87.5 g/mole was found (calculated 87.0), which is well within the experimental error.

The vapor pressure of NF_3 was determined from -136 to -108 C, using thirty measurements which were fitted to the following equation by the method of least squares on the IBM 7090:

$$\log p_{\text{mm}} = 7.86279 - 917.087/T$$

The extrapolated boiling point is -89.1 C, $\Delta H_V = 4195 \pm 26$ cal., and the Trouton's constant is 22.8.

The melting point was determined by observing the melting of a ring of solid NF_3 on the walls of an ampoule. It was found to be -161.5 ± 1.0 C. The low boiling and melting points are in marked contrast to the usually high ones observed with amine oxides, substantiating the thesis that the compound is not a true amine oxide (Ref. 1). The high polarity of amine

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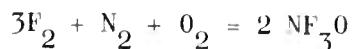
oxides tend to markedly increase the molecular attraction, as for example, the case of trimethyl amine oxide which melts at 208 C, while the isomeric trimethyl hydroxylamine boils at 30 C (Ref. 4).

SYNTHESIS OF NF₃O

A good deal of effort was expended in the synthesis of NF₃O in order to improve our understanding of the electrical discharge technique. First, the present methods for the preparation of laboratory quantities of NF₃O were inadequate, and, second, the technique might be adaptable to the synthesis of other oxidizers. Two methods were investigated, one using nitrogen trifluoride-oxygen-helium mixture at -183, and the other employing a fifty-fifty mixture of fluorine and air at -196. The latter method has proved to be best with as much as 0.3 g being made per hour.

The geometry of discharge cell has proved to be of critical importance. With the modified U reactor shown in Fig. 1, the yields have been approximately tripled. It is felt that the success of the new reactor is due to greater efficiency of contact between the gas stream and the glow discharge, and to improved cooing of the reaction zone. It is hoped that this design will also be of help in our synthesis of new binary N-F compounds.

The pressure at which the reaction is run is also a major factor. Pressures below 50 mm tend to decrease the amount of NF₃O formed, while higher pressures are of no further benefit. It is interesting to note that variations in electrode separation, between 5 to 8 cm, do not change this fact, even though an increase in electrode distance has generally the same effect on the discharge potential as an increase in pressure. It is not surprising that the rate of formation of a pentatomic compound from the elements should increase with pressure:

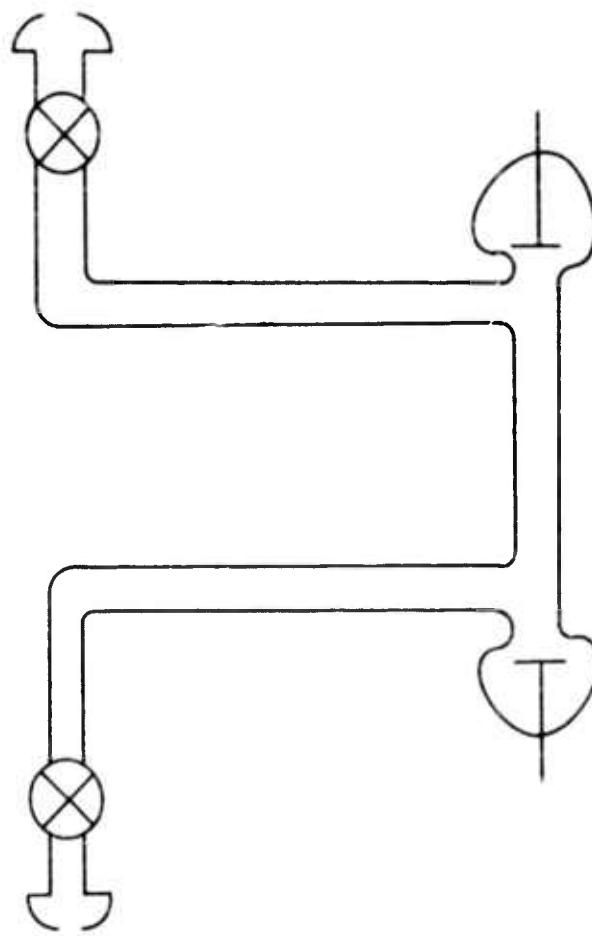


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4

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ELECTRICAL DISCHARGE CELL

Figure 1 . Modified U Reactor

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5

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but the fact that a maximum exists is harder to interpret. A reasonable explanation lies in the observation that the discharge becomes more concentrated, i.e., goes from a diffuse glow to more of a continuous spark, as pressure is increased. This may tend to result in poor contact between the reactants and the excited zone of the discharge.

BINARY N-F COMPOUNDS

It has been previously reported (Ref. 3) that a mixture of nitrogen and fluorine reacted in an electrical discharge to yield new compounds, possibly unknown binary N-F ones. These compounds have been designated as Compounds A and B. Both were condensable at -142°C and Compound A absorbed in the infrared at 13.6 while Compound B absorbed at 14.2 microns. Upon standing, the mixture yielded only Compound A absorbing at 13.6 microns.

Two attempts at reproducing these compounds under similar conditions using fluorine-nitrogen mixtures were not successful. In the first case the products were identified as NF_3^0 , COF_2 , SiF_4 , NO_2 , and fluorocarbons. The second run yielded NF_3^- , COF_2 , SiF_4 , NO_2 , and CF_4 . An all-Pyrex gas circulating system was used and the products were trapped continuously. An air leak in the reactor was noted during the first run and may explain the formation of NF_3^0 rather than NF_3^- or other binary N-F species.

However, a mixture of nitrogen trifluoride and nitrogen did yield Compound A. Electrical discharge with recycling of the reactants produced a mixture containing a compound (or compounds) condensable at -126 and absorbing in the infrared at 12.7 and 13.65 microns (Fig. 2). The 12.7 peak is perceptible only when the 13.65 peak is large (percent transmission less than 10 percent). It may be due to a different compound, although it has not

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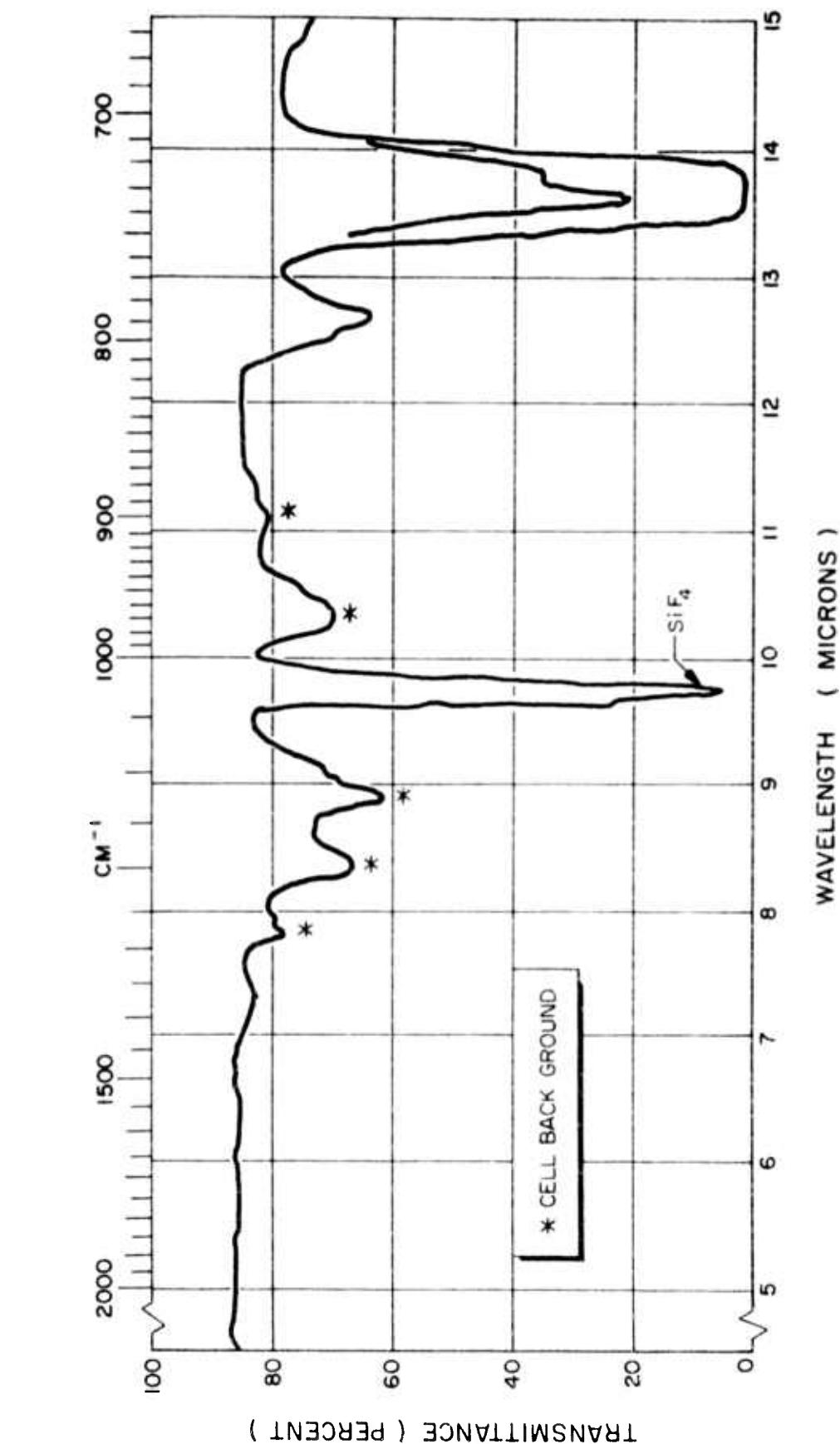


Figure 2 . Infrared Spectrum of Mixture of Compounds
Produced by Electrical Discharge

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7

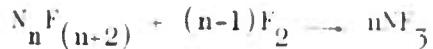
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been observed independently and it appears to decay together with the 13.65 peak. Both absorptions are reproducible after the mixture is allowed to stand at -196°C, but disappears slowly at ambient temperature.

Mass spectrometric analysis of Compound A gives a very complex spectrum, although the only suspected impurities are Cl₂ (yellowish solid at -142°C) and SiF₄. These two impurities arose from attack on the Halocarbon grease and the Pyrex system. These impurities are in evidence in the mass spectrum as well as minor quantities of -NF and -NF₂ type compounds. An extremely reactive oxidizer such as chlorine trifluoride is known to give a complex mass spectrum showing but minor quantities of oxidizer.

Reaction without recirculation of NF₃-N₂ mixtures gave only minute quantities of material condensable at -142°C which had a small infrared absorption at 13.6 microns. In addition, nitrogen trifluoride to nitrogen ratios of 0, 5:1, 5:2, 2:1, and 5:5 were investigated. The experiment with only nitrogen trifluoride yielded very little binary N-F compound, whereas the amounts of Compound A increased with the proportion of nitrogen present. It is believed that relatively large amounts of fluorine formed from nitrogen trifluoride reduce the amount of Compound A formed unless sufficient nitrogen is also present, as shown by the following type of reaction:



Fluorine and nitrogen are apparently formed from nitrogen trifluoride in an electrical discharge. This should lead to a volume increase of one hundred percent if complete decomposition occurred. An equimolar nitrogen

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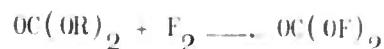
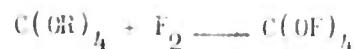
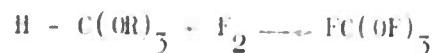
trifluoride-nitrogen mixture passed through an electrical discharge should give a volume increase of fifty percent. This volume increase was detected experimentally by an increased flowrate measured after the gases had passed through a -196°C trap.



Small amounts of condensable products were found at -196°C. In view of these findings, future reactors will employ an excess of nitrogen.

DIRECT FLUORINATIONS

Since thermodynamic calculations show that O-F compounds have considerable promise as high energy oxidizers, an investigation has been initiated into their synthesis by direct fluorination, the ultimate goal being compounds such as C(OF)_4 , FC(OF)_3 , and OC(OF)_2 . Compounds which readily suggest themselves as candidates for fluorination are: triethyl and trimethyl orthoformate, tetraethyl and tetramethyl orthocarbonates; diethyl and dimethyl carbonates; and metallic carbonates such as sodium and silver carbonate.



R-3071-1

9

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The direct fluorination of trimethylorthoformate at 95 to 98 C has been reported by Armour (Ref. 5) to give a rather complex mixture of products. Under similar conditions, we have confirmed their results.

However, when low-temperature fluorination at -80 C was employed, indications of a new compound were found in the O-F region of the infrared spectrum. Due to the small amounts involved, this observation awaits reconfirmation in a larger scale experiment.

R-3071-1

10

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EXPERIMENTAL DETAILS

PHYSICAL AND CHEMICAL PROPERTIES OF NF₃O

All experiments were run on a sample of NF₃O which had been purified by vapor phase chromatography, and which was of better than 99 percent purity by infrared and mass spectral analysis.

Oxidation Equivalent

About 2 cc of NF₃O was measured into an ampoule, and an excess of aqueous potassium iodide, acidified with acetic acid, was introduced. Care was taken to have all solutions made with deaerated distilled water, and to introduce the solution in a manner to exclude all traces of air. After shaking for 5 min, the ampoule was connected to a vacuum line, and the ullage carefully evacuated until the solution started to boil. The ampoule was removed, shaken, and the procedure repeated three times. The I₃⁻ solution was then titrated in the usual manner with thiosulfate. The results are given below:

NF ₃ O <u>m moles</u>	S ₂ O ₂ ⁼ <u>meg</u>	NF ₃ O <u>equiv/mole</u>
0.129	0.414	3.21
0.133	0.435	3.25
Average		3.23

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In one experiment, when the NO was removed from the mixture, the gases were trapped at -196 C. After fractionation to separate the water from the NO, it was found that 70 percent of the NO had been recovered. It was too small a quantity to give an infrared spectrum directly since NO is a weak absorber, but when air was introduced NO_2 was formed instantly and easily identified.

Molecular Weight Determination of NF_3O

The molecular weight was determined by the gas density method. These data are reported below:

Weight Sample, <u>g</u>	Volume STP, <u>cc</u>	Molecular Weight, <u>g/mole</u>
0.0344	8.84	87.2
0.0404	10.3	<u>87.8</u>
Average		87.5 (calculated 87)

Vapor Pressure of NF_3O

Temperatures below -108 C were measured with an ethylene vapor tension thermometer, and those above with a carbon dioxide thermometer. These data are listed in Table 1.

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TABLE 1

VAPOR PRESSURE OF NF₃O

Temperature, K	Pressure Measured, mm	Pressure Calculated, mm
137.4	16.0	16.1
137.7	16.0	16.7
138.2	17.0	17.6
139.0	19.0	19.2
140.3	23.5	22.1
141.2	24.0	24.3
142.4	27.0	27.6
142.2	27.5	27.1
144.0	33.0	32.6
144.6	34.5	34.4
145.8	39.0	39.1
148.2	49.5	49.4
150.0	61.5	58.5
151.1	67.5	64.9
151.9	71.0	69.8
152.7	80.0	82.1
153.7	80.0	75.1
154.4	87.0	87.4
154.9	88.5	91.4
157.4	110.5	114.4
158.0	120.5	119.6
158.0	120.5	119.6
158.5	124.0	126.6
158.7	124.0	124.6
159.9	141.0	139.9
160.4	144.0	145.7
161.4	154.0	158.2
161.9	164.5	164.9
162.3	165.5	170.1
162.7	180.5	175.5

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Data were fitted to the following equation by the method of least squares:

$$\log p = 7.86279 - 917.087/T$$

The standard deviation from this equation is ± 2 mm.

Melting Point

About 0.2 g NF_3O was frozen at -196 C in a ring on the walls of an ampoule. The ampoule was then immersed in a bath of liquefied city gas in a clear dewar. Liquefied city gas, a mixture of 86 percent methane and 14 percent ethane, is a colorless liquid from -196 to temperatures above -140 , and seems to be ideal for such measurements, provided good ventilation is available. The methane boils off slowly allowing the temperature of the bath to rise steadily and smoothly. The melting point was taken to be that temperature at which the solid became transparent. The temperatures were measured with an iron constantan thermocouple calibrated against liquid nitrogen (-196), liquid oxygen (-183) and at -157 C against an ethylene vapor tension thermometer. Two measurements gave -160.5 and -162.5 , average -161.5 ± 1.0 C. The melting range of the samples was less than 1 C.

PREPARATION OF NF_3O

A 15 kv, 30 ma luminous tube transformer was used as a power source. The improved U-type discharge cell, shown in Fig. 1, had the electrodes 5 cm apart. A 60-liter stainless steel tank was filled to atmospheric pressure with a fifty-fifty mixture of fluorine and air, and used as a reservoir for the experiments. The gas flow to the cell was regulated by means of a needle valve, and the pressure was kept constant by a manostat downstream

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from the reactor. The manostat was a long bubbler (50 cm) filled with "Fluorolube" oil, and worked quite well in monitoring gases containing fluorine. The discharge cell was kept immersed in liquid nitrogen throughout the run. At the end of a run, the cell was allowed to warm up with pumping, through a -142 and -196 trap. The O_2F_2 was largely retained in the -142 trap, along with N_2O_2 when formed. The -196 trap contained NF_3 , NF_5O , SiF_4 , nitrogen oxides, small amount of O_2F_2 , and some fluorocarbons, including CF_4 . The NF_5O was further purified by fractionation under high vacuum through -142, -183 and -196 traps. Almost all the NF_5O was retained in the -183 trap, free from NF_3 , but still contaminated with some SiF_4 , N_2O , and traces of fluorocarbons. The SiF_4 could be removed with sodium or potassium fluoride, but the other impurities could only be removed by vapor phase chromatography (Ref. 1).

The runs employing NF_3 , O_2 , and helium mixtures were performed similarly, except that the cell was kept at -183°C (liquid oxygen), and the pressure during the run was 1 to 2 mm. Very much the same products were recovered: starting materials, O_2F_2 , NF_5O , SiF_4 , and nitrogen oxides. FN_2 and FN_2O_2 were sometimes formed, and traces of fluorocarbons were always present.

A summary of the experimental findings is given below:

<u>Reactants</u>	<u>Cell</u>	<u>Pressure, mm</u>	<u>T, °C</u>	<u>NF_5O, percent</u>
NF_3-N_2 -He	1	1 to 2	-183	3
F_2 -Air	1	50	-196	4
F_2 -Air	1	55	-196	3
F_2 -Air	1	20	-196	~ 0
F_2 -Air	2	50	-196	10

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Cell No. 1 refers to the design used earlier (Ref. 3), and No. 2 to the improved design. The yields are based on oxygen since it is present in less than stoichiometric amounts.

BINARY N-F COMPOUNDS BY ELECTRICAL DISCHARGE

The experiments are summarized in Table 2. Fluorine and nitrogen were used from commercial sources without further purification. Nitrogen trifluoride was purified by passing the gas through a -142°C trap and condensing the gas at -196°C. The power source for the electrical discharge was a 15 kv, 30 ma ac transformer. The electrodes separation was 8 cm in all cases.

The volume of the closed reactor system was 650 ml, reactant gases being continuously recirculated. Recirculation was effected by a magnetically driven all-glass gas circulating pump, the rate being approximately 2000 ml/min. The reaction zone was cooled in runs 1 to 8 by circulation of coolant through 1/2-in. stainless steel electrodes and a condenser jacket. The entire reaction zone was immersed in coolant in run 9. The coolant in runs 1 through 6, and run 9, was trichloroethylene maintained at -80°C; in runs 7 and 8, water was used at 25°C. No gas recirculation was employed in 7, the flow pressure being maintained at 55 mm by an oil manostat.

The products in all runs were trapped immediately after the reaction zone. When nitrogen and fluorine were used as reactants, in runs 1 and 2, a -196°C trap was used. When nitrogen trifluoride was a reactant, a -142°C trap was necessary. Compound A may be partially trapped at -126°C and will pass through a -112°C trap. The portion passing through the -126°C trap is completely condensed at -142°C. The infrared spectra of the -126 and -142°C fraction appear identical.

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TABLE 2
PREPARATION OF COMPOUND A

Run	Reactant Composition	Pressure Range, mm	Circulation	Trap Temperature, C	Time, hr	Amount of Compound A, cc	Products
1*	F ₂ :N ₂	2:1	20 to 60	yes	-196	2	NF ₃ O, COF ₂ , N ₂ O, NO ₂ , SiF ₄ , C-F
2	F ₂ :N ₂	5:1	15 to 85	yes	-196	1	none
3*	NF ₃ :N ₂	5:2	15 to 25	yes	-142	3	< 0.2
4	NF ₃ :N ₂	2:1	25 to 50	yes	-142	5	≤ 0.5
5	NF ₃ :N ₂	5:5	15 to 60	yes	-142	5	≤ 1.0
6	NF ₃ :N ₂	5:5	15 to 60	yes	-142	3.5	≤ 0.8

* Reactor Air Leak

R-3071-1

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TABLE 2
(Continued)

Run	Reactant Composition	Pressure Range, mm	Circulation	Trap Temperature, °C	Time, hr	Amount of Compound A, cc	Products
7	NF ₃ :N ₂ 1:1	55	no	-142 to -190	3	≤ 0.1	Compound A, NF ₃ , COF ₂ , NO ₂ , SiF ₄ , CF ₄
8	All NF ₃	15 to 40	yes	-142	3.5	< 0.1	Compound A, COF ₂ , NOCl, NO ₂ , SiF ₄
9	All NF ₃	40 to 60	yes	-142	2.5	none	NOF, NO ₂ , SiF ₄

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Because of the presence of SiF_4 and Cl_2 impurities, no accurate estimate could be made of the actual amounts of Compound A prepared. No attempts at purification other than fractional condensation were made. Upon decomposition of Compound A at ambient temperature, no new infrared absorptions were observed.

DIRECT FLUORINATIONS

Vapor Phase Fluorination

Two vapor phase fluorinations were carried out in a reactor (Fig. 3) packed with copper turnings. A stream of nitrogen was bubbled through trimethyl orthoformate (Eastman) heated to 95°C, and the vapors were introduced into the reactor at the topmost port while the fluorine was slowly fed in by the opposite port. The gaseous products exited through the bottom port to a -156°C trap. The heat of reaction raised the reactor temperature from room temperature to 140°C. The reactor was found to contain 3 ml of a brown liquid which oxidized KI but which on infrared analysis showed only the starting material. The gases trapped in the -156 trap had a complex infrared spectrum, being apparently a mixture of fluorocarbons.

A second run was aborted shortly after the start due to a leak in the system. Examination of the volatile products failed to reveal any new species.

Low-Temperature Fluorinations

A new reactor (Fig. 4) was designed that could be immersed in a trichloroethylene-dry ice bath. In this way the trimethyl orthoformate was kept as a solid at -80, and the fluorine was chilled before contact by

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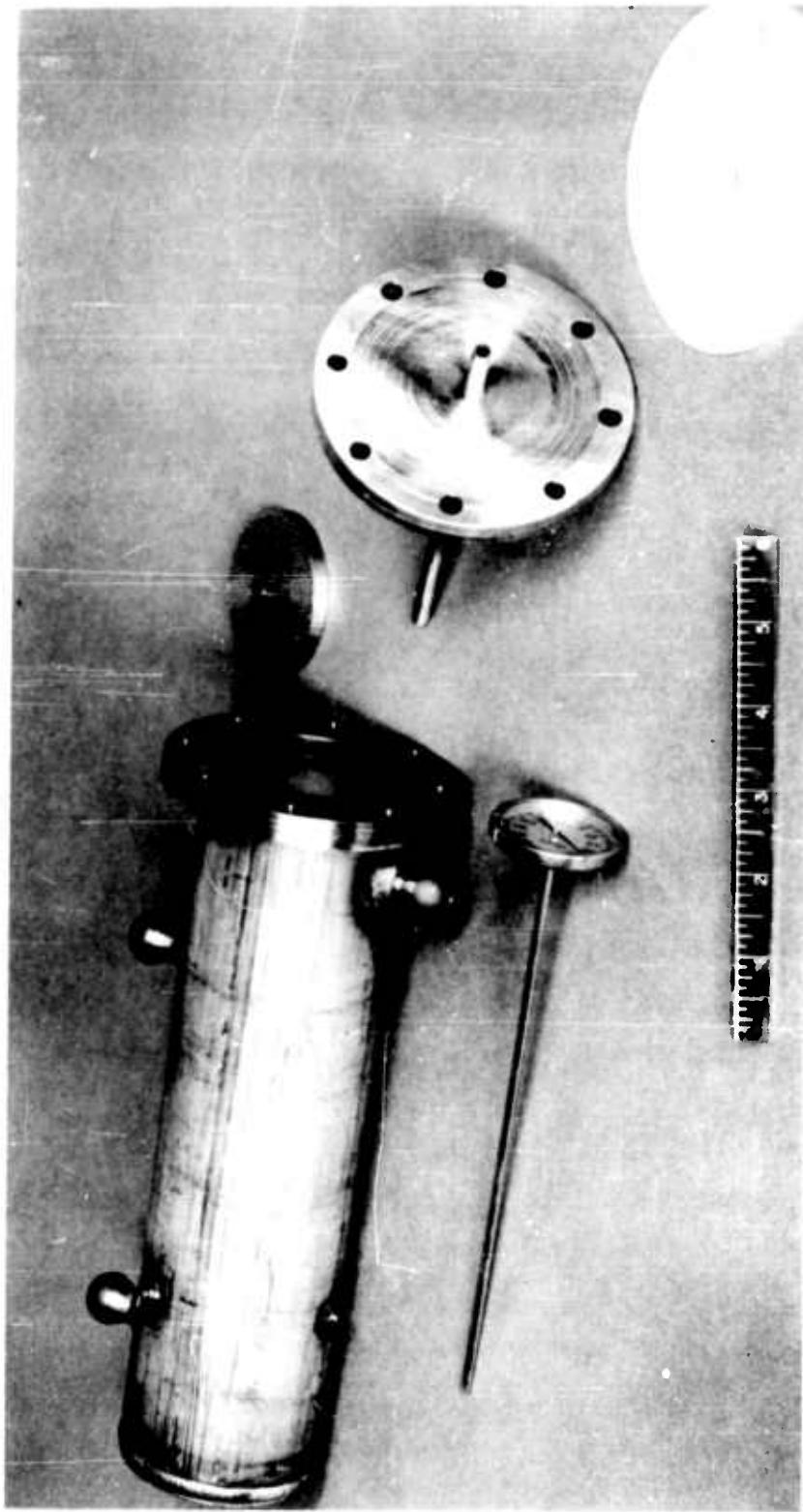


Figure 3 . Gas Phase Fluorination Reactor

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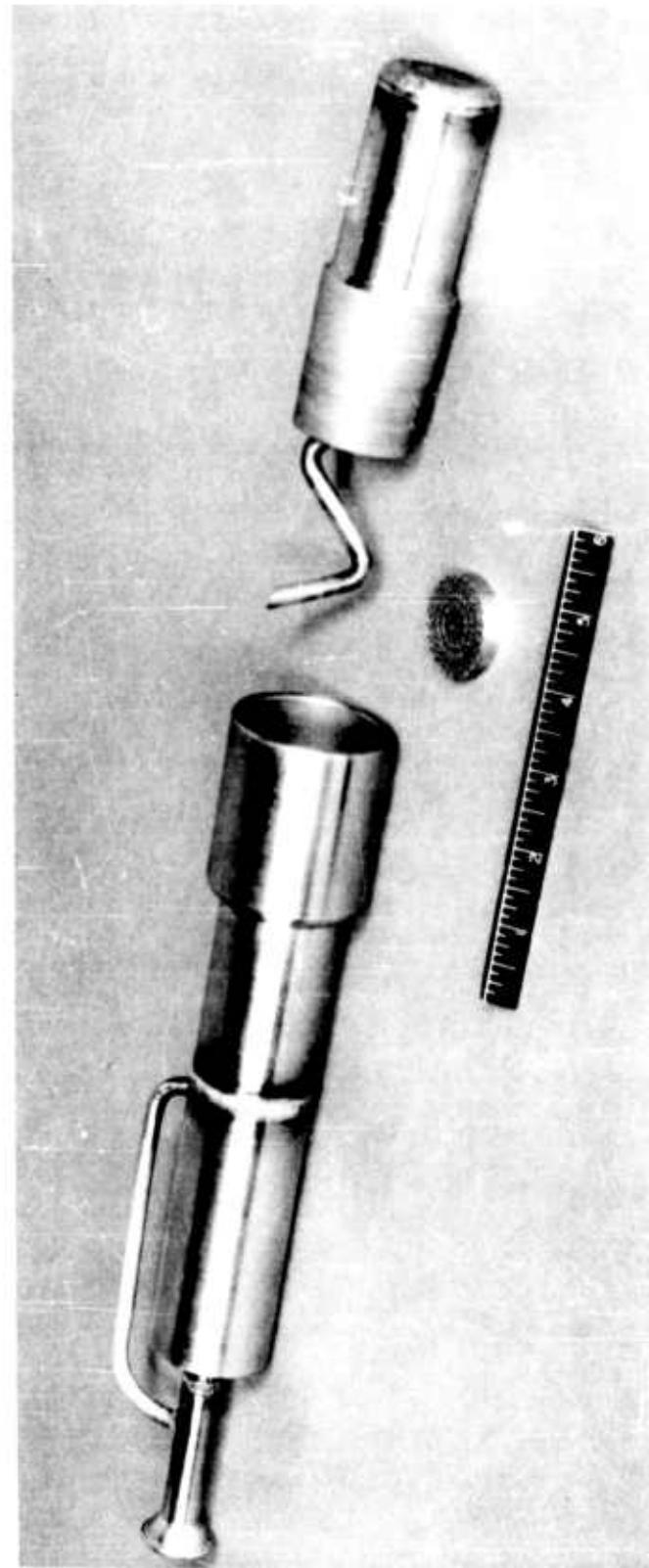


Figure 4 . Fluorination Reactor for Low Temperatures

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entering through the bottom of the reactor. The trimethyl orthoformate was solidified at -196 C, broken into small lumps, and transferred to the chilled reactor.

Two fluorinations were performed. In the first one, no oxidizing materials were formed, while in the second the residual liquid in the reactor not only had oxidizing power, but the volatile fraction had unknown absorptions in the region of 10 to 13 microns in the infrared, where an O-F bond may be expected to absorb.

R-3071-1

22

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SUMMARY AND CONCLUSIONS

Direct chemical evidence for the empirical formula NF_3O has been obtained from the quantitative reduction with iodide ion. The vapor pressure equation and melting point of pure NF_3O have been obtained, thus completing the characterization of its important physical properties. Future work will be directed at the study of the reactions of NF_3O to define its chemical properties and potential as an intermediate.

The new compound, designated as Compound A, previously obtained through the electrical discharge of nitrogen-fluorine mixtures, has now been obtained from mixtures of NF_3 and nitrogen. Work will continue on this extremely interesting compound to elucidate its structure.

The direct fluorination of trimethyl orthoformate at -80°C has given volatile products which absorb in the infrared in the region expected for O-F bonds. The work will be continued to see if new oxidizers have in fact been made by this method.

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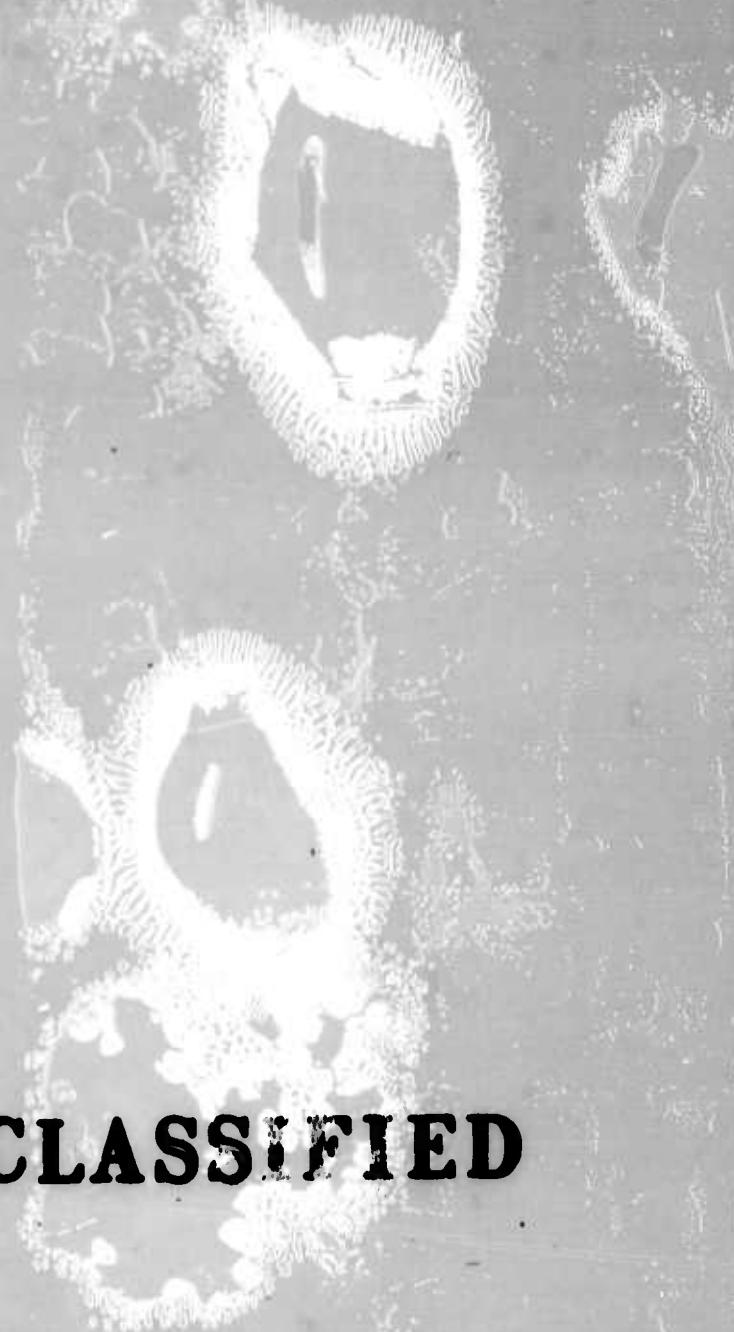
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